The Helmholtz Free Energy of Water/Ammonia Mixtures

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Mixtures of water and ammonia are widely used in absorption refrigeration applications. Recently, this mixture has been proposed as a possible working fluid in the Kalina cycle which is suitable in heat recovery units. For reliable design, accurate knowledge of the thermodynamic properties are essential, not only for VLE-properties (p, T, x, y) but also for volumetric and caloric properties in the whole range of the thermodynamic surface.

The present work describes a fundamental equation of state approach in terms of the Helmholtz free energy which has been developed recently. It uses state-of-the-art pure fluid equations and is supplemented with a departure function which accounts for nonideal mixture behavior. The fundamental equation of state approach gives a thermodynamically consistent description of one-phase and two-phase properties. Thus, all properties (VLE and single-phase) can be calculated from a single mathematical expression using exact thermodynamic relations.

The Helmholtz free energy model has been applied to the mixture water/ammonia. It is based on available literature data covering the whole range of composition. VLE-properties between the triple line and the critical line and properties in the liquid and vapor region can be calculated from the new fundamental equation of state. Typical uncertainties are ± 0.01 for liquid and vapor compositions, $\pm 0.3\%$ for densities and ± 200 J/mol for enthalpies almost corresponding to the uncertainty of experimental input data. Furthermore, the equation shows reasonable behavior when extrapolated into the supercritical area.